
Capture of carbon dioxide by solid amine sorbents

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Abstract: The reaction of tetraethylorthosilicate (TEOS) with γ -aminopropyltriethoxysilane (APTS) has produced stable solid amine sorbents for the capture of carbon dioxide. The resulting amine-enriched silicon sorbent (SBA-15) has been proven to be competitive with existing environmental CO₂ controlled life sorbents based on the immobilised amine technology. XPS analysis has indicated that the amine groups (N1s Peak) were incorporated onto the surfaces of this amine-based sorbent in the range of 7%. The performance of the SBA-15 was comparable to the commercially available immobilised amine sorbent (IAS).

Keywords: amine sorbent; capture; carbon dioxide.

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Biographical notes: M.L. Gray, Y. Soong, K.J. Champagne, H.W. Pennline and J. Baltrus are Researchers who work out of the US Department of Energy's National Energy Technology Laboratory in Pittsburgh, PA. All are involved in developing technologies for the removal of carbon dioxide from gas streams.

R.W. Stevens, Jr., R. Khatri and S.S.C. Chuang are Researchers from the University of Akron who have collaborated with the NETL researchers in this particular project.

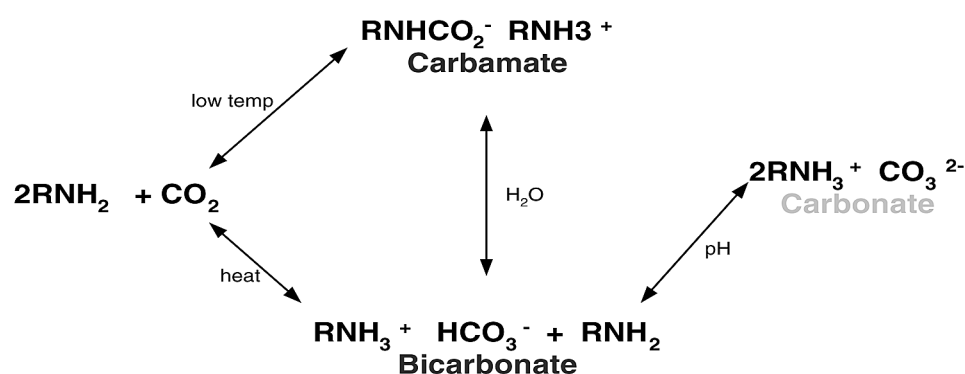
1 Introduction

The concentration of CO₂ in the atmosphere is promoted by the combustion of fossil fuels for the generation of electricity. Capturing CO₂ from flue gas streams is an essential step for the carbon management for sequestering CO₂ from our environment. The capture step is projected to be a significant cost and energy concern in a carbon sequestration scenario. Current storage technologies [1] being considered for CO₂ sequestration include disposal of CO₂ in deep oceans, in depleted oil and gas fields, in deep saline formations (aquifers), and in unmineable coal-bed seams. However, the current cost for the utilisation of these types of technologies has proven to be too expensive. Consequently, reducing the cost for the capture of CO₂ will be a critical step in the overall carbon management programme.

The capture and separation of CO₂ can be achieved by using solvents, cryogenic techniques, membranes, and solid sorbents. The large-scale operation of these technologies is energy intensive when applied to capturing CO₂ in a dilute stream, such as flue gas, which consists of 15 volume % CO₂ for most coal combustion systems. Amine-based, wet scrubbing systems have been proposed as capture techniques for CO₂ removal from flue gas, but are energy intensive due to the large amount of water needed in these systems. Excessive water is required because of the mechanism and corrosiveness of such amines as monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA) in these aqueous-based, CO₂-capture systems. The proposed reaction sequences [2] in aqueous systems using primary, secondary, and tertiary alkanolamines reacting with dissolved CO₂ are shown below.

According to Figure 1, the majority of the CO₂ captured will result in the formation of bicarbonate in these liquid amine capture systems. In aqueous media, there is a requirement of 2 moles of amine/mole of CO₂ for the formation of stable bicarbonate compounds resulting in the capture of CO₂.

Figure 1 Proposed reaction sequence for the capture of carbon dioxide by liquid amine-based systems



Solid-amine CO₂ sorbents should have similar reactions with gaseous CO₂, water vapour, and the amine site on its surface. As a result, immobilised amine sorbents (IAS) are being used in aircraft, submarine, and spacecraft technologies [3–5]. However, the cost of these

sorbents is too expensive for large-scale applications in the utility industry. Thus, SBA-15, a novel amine-based sorbent, is currently being examined as a cost efficient sorbent for the capture of CO₂ from gas streams containing moisture. Consequently, a comparison study of the SBA-15 and the IAS sorbents will be discussed within this communication.

2 Experimental procedures

2.1 Preparation of SBA-15

SBA-15 was prepared by using TEOS (tetraethylorthosilicate) as a silica precursor, Pluronic P123 (PEO₂₀PPO₇₀PEO₂₀, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) as a template, TMB (1,2,3-trimethyl benzene) as an expander, and HCl to control pH. [6,7] The specific steps for preparation of SBA-15 consist of:

- 1 dissolving 4.0 g of Pluronic P123 in 30 g of water and 120 ml (2.0 M) of HCl solution at room temperature
- 2 mixing the resultant solution with 30 g TMB at 35°C for 2 h
- 3 adding 8.5 g TEOS into the resultant homogeneous solution and stirring it at 35°C for 22 h
- 4 ageing the solution without stirring at 120°C for 24 h
- 5 filtering the aged solution and calcining the resultant solid particles in flowing air at 270°C/min to 500°C and holding it at 500°C for 6 h [6–8].

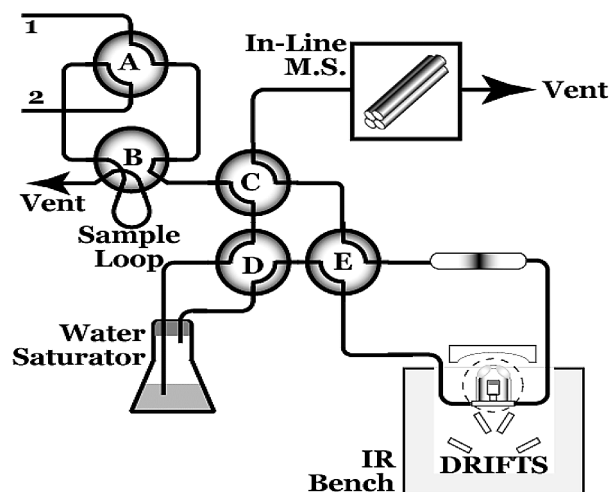
The surface area of the SBA-15 was determined by N₂ BET measurement at 77 K.

2.2 Preparation and characterisation of the sorbent

SBA-15 grafted with γ -aminopropyltriethoxysilane (APTS) was prepared by impregnating an APTS/toluene solution into SBA-15 [9]. The impregnated sample was heated at 423 K for 20 h in a vacuum oven to obtain APTS-SBA-15. ATPTS-SBA-15 denotes the SBA-15 grafted with APTS. X-ray photoelectron spectra (XPS) of SBA-15 and APTS-SBA-15 were determined by a PHI5600ci instrument with monochromatic Al K α X-rays.

2.3 CO₂ capture capacity

The chemical CO₂ capture capacities were determined by the combination of Temperature Programmed Desorption (TPD) and Mass Spectroscopy (MS) analyses. The adsorption of CO₂ was achieved in the presence of moisture at 25°C, and the total desorption of CO₂ was achieved over the temperature range 30–60°C. The composition of the experimental gas stream used in these test runs was 10% CO₂/H₂O/He. The detailed operating conditions for this procedure were previously described in the literature [9,10]. The experimental set-up for these test runs is shown in Figure 2.

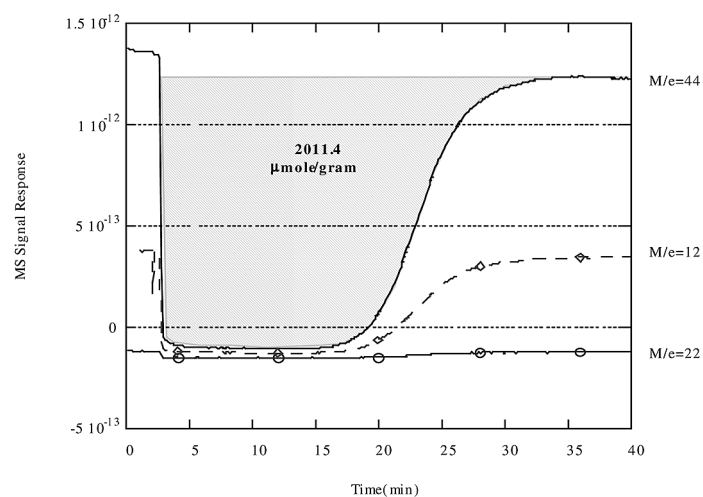
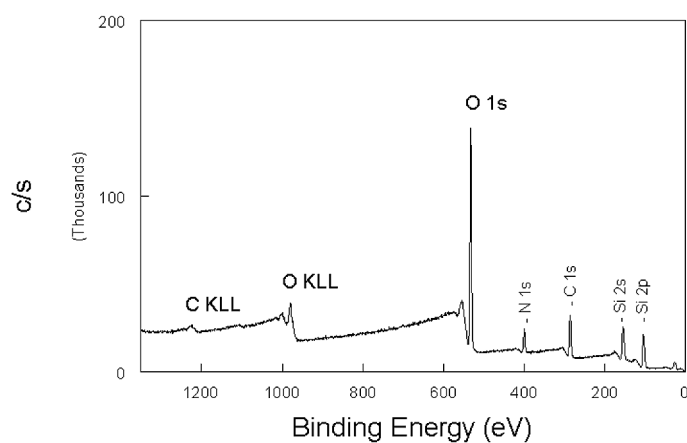
Figure 2 Experimental set-up for TPD/MS analysis

2.4 XPS analysis

The amount of nitrogen (N1s Peak) on the surface of the amine-enriched sorbent was determined by XPS analysis. The XPS analysis was conducted at 1×10^{-8} torr with the surface analysis depth range from 30 to 50 angstroms. Under these conditions the chemically and the strongly adsorbed amines can be determined for each of the CO₂ capture sorbents. The details of this experimental procedure have been reported in the literature [11].

3 Results and discussion

Initially, the performance of the prepared amine-enriched silicon sorbent (SBA-15) was compared to an existing industrial solid amine sorbent (IAS). Each sorbent was placed in a 10% CO₂/H₂O/He stream and TPD and MS analyses were conducted to determine the performance of these CO₂ capture sorbents. The adsorption/desorption of CO₂ for these sorbents were determined over the temperature range 25–60°C. Typical TPD/MS and XPS spectra are shown in Figures 3 and 4. According to the TPD/MS analysis, all of the sorbents were successful in the capture of CO₂ from the moist experimental gas streams. The comparison of the CO₂ capture performances and XPS results for these sorbents are summarised in Table 1.

Figure 3 Typical TPD mass spectra of SBA-15**Figure 4** Typical XPS spectra of SBA-15 sorbent**Table 1** TPD CO₂ desorption and XPS data of the amine-enriched sorbents

<i>Sorbent</i>	<i>μmol/g CO₂ captured</i>	<i>XPS % nitrogen</i>
SBA-15-fresh	2011.4	7.1
SBA-15-1st regeneration	1908.5	NA
SBA-15-2nd regeneration	1748.3	NA
IAS-fresh	1603.9	17.7
IAS-1st regeneration	1922.6	NA
IAS-2nd regeneration	1528.1	NA

As shown in Table 1, the SBA-15 had a lower % nitrogen value of 7.1 versus the IAS % nitrogen value of 17.7. Despite the differences in the nitrogen values, the sorbents had similar average CO₂ capture capacities. The SBA-15 and the IAS sorbent were regenerated at 60°C over two additional test runs and the average CO₂ capture capacity values were 1889 µmol/g and 1820 µmol/g, respectively.

The CO₂ capture capacity of these sorbents is dependent on a couple factors:

- basicity of the amine site for the formation of the carbamate ion (refer to Figure 1)
- accessibility, distribution, and orientation of the amine sites
- surface area of the sorbents.

Since the SBA-15 and IAS had similar basicities and surface areas of 227 versus 219 m²/g, the potential major factors in affecting the performance of these sorbents are the accessibility, distribution, and orientation of the amine sites within the structure of these sorbents. According to the patents [4,5], the preparation of the IAS requires the evaporation and/or adsorption of the amines into the pores of the solid substrate which may lead to multi-layering, uneven distribution, and limited access to all of the amine sites required for the capture of CO₂. However, the amine sites incorporated into the structure of the SBA-15 are chemically bonded or strongly absorbed to the OH sites on the surface, which creates a more uniform distribution of the amine sites. Consequently, the majority of the amine sites on the SBA-15 are accessible for the capture of CO₂. Thus, the surface area, accessibility, distribution and orientation of the available amine sites all have the potential of playing an important role in the performance of these solid amine CO₂ capture sorbents.

4 Conclusion

Preliminary results indicate that the SBA-15 sorbent is comparable to the IAS sorbent which is currently being used as an environmental CO₂ controlled life sorbent. The surface area, % nitrogen, and distribution and orientation of the amine sites all play an important role in the performance of these solid amine CO₂ capture sorbents.

5 Disclaimer

Reference in this report to any specific commercial process, product or service is to facilitate understanding and does not necessarily imply its endorsement or favouring by the USA Department of Energy.

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